

ADJUSTMENT OF AUTOMATED EMISSION MONITORING SYSTEMS

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ABSTRACT

For continuous control of large sources automated emission monitoring systems for dust and different gaseous pollutants are used. These analysers have to be calibrated, depending on the national regulations after the installation and in regular intervals by means of independent reference methods, e.g. every three years. During the intervals of calibration and functional controls the operator has to maintain his analytical equipment for himself. One of these tasks is adjustment of analysers. All analysers are no absolute measuring systems. Generally drifting of zero and span (reference point) can be noticed. The stability of different systems can vary considerably. Therefore it is necessary to adjust zero and span point of analysers in regular intervals. This paper describes systems for adjustment of dust and gas analysers. It starts for gas analysers with conventional manual technique with span gases followed by automated systems still using span gases and describes modern systems according different principles, e.g. analysers only with adjustment of zero or systems working with cuvettes, filled with the gas to be measured. The results of long term studies of these systems are reported.

1. INTRODUCTION

Continuous emission monitoring - from the instrumentation point of view - is derived from the measurement technology for operating analyses. In this area continuous gas analysis processes had already been developed, even before any legally-specified emission monitoring had hardly been thought of, e.g. due to the invention of the first photometer which operated according to the NDIR method [1]. Before emission monitoring, continuous gas analysis was already being carried out in various areas of industry such as the chemical industry, in power stations, steel manufacture or in mining.

The following general comments are based on the developments in Germany but they may well be similarly relevant for other European countries.

2. THE DEVELOPEMENT OF CONTINUOUS EMISSION MEASURING TECHNOLOGY

The beginnings of continuous emission monitoring in the FRG took place from 1966 onwards in North-Rhine Westfalia [2], and later in the other Federal States as well. At that time a complete emission measuring device consisted of a photoelectric dust measuring unit, an SO₂ measuring unit, a CO₂ or O₂ measuring device, a temperature measuring instrument and a multiple line recorder. In addition the steam quantity was also measured as a characteristic operating parameter.

The TA Luft legislation (Federal Regs. for Air Purity) of 1974 [3] extended the possibility of monitoring a whole series of other components: NO_x, CO, C_xH_y, gaseous inorganic chlorine and fluorine compounds (HCl, HF), H₂S and chlorine.

In the area of gas analysis instrumentation for these "classic hazardous substances", about which we are talking here, it has been shown very clearly that it is only because of the legal requirements that further developments in measuring technology were first initiated. When the TA Luft legislation appeared in 1974 it was not clear whether the new requirements could be fulfilled with the existing measuring equipment, e.g. in the case of NO_x. The legal requirements however gave the measuring

instrument manufacturers the necessary incentive within the scope of the market economy to develop new and improved measuring instruments. To remain with the example of NO_x: In 1974 a chemiluminescence measuring instrument was just able to meet the new requirements. In the course of time there came more and more new developments onto the market, so that in Germany today there are more than 35 authorised NO and NO₂ measuring instruments both as single units and as multi-component measuring instruments. And in this we have not even counted the different variations of each device. The measuring technology used for these components has undoubtedly shifted towards the photometric process. This trend has continued with the appearance of the 13th BImSchV (Large furnaces order) in 1983 [4] and the 17th BImSchV (order on incineration plants for waste and similar combustible material) 1990 [5]. In total at present there are certainly over 100 authorised emission measuring devices for gases (not including O₂ devices, multi-component measuring devices only counted as one).

The relevant regulation, to which the performance of the measuring technology has to be oriented today, is the 17th BImSchV with its low limit values. The actual concentrations arising on the plants is mostly well below these emission limit values. As the 17th BImSchV and the directive 2000/76/EC [6] of the European Parliament and the Council concerning the incineration of wastes were published, there were many questions concerning continuous emission monitoring and the evaluation thereof, which have in the meantime long since been resolved.

Following the appearance of the 17th BImSchV it was again apparent in Germany – as already following the publication of the TA Luft legislation in 1976 and the 13th BImSchV in 1983 - that the demands of the legal stipulations stimulates the development of the measuring technology, since a market was now expected by the manufacturers.

In the following table are shown the limit values for the components to be continuously measured as given in directive 2000/76/EC.

Tab.1: Limit values of Directive 2000/76/EC

Component	Daily limit value mg/m ³	Half-hourly limit (100 %) A mg/m ³
NO _x	200	400
CO	50	100
Total dust	10	30
Total C(TOC)	10	20
HCl	10	60
HF *	1	4
SO ₂	80	200

*) HF can be dropped if it is ensured that the HCl limit is not exceeded. Since this is normally the case for waste incineration we will not deal any further with HF in this paper.

In addition the operating variables of O₂, humidity, pressure and combustion chamber temperatures must be measured. For all the components mentioned there are already practically-tested measuring devices available.

3. THE MOST IMPORTANT MEASURING PRINCIPLES

In terms of measurement strategy there are two fundamental processes: In-situ and extractive

measuring technology.

The in-situ measuring technology is characterized in that the measurement is made directly in the flue gas channel. The measured values are therefore initially always determined as relative to the actual flue gas condition and then converted by means of the moisture content, pressure and temperature to the standard dry condition. Except for a few exceptions this procedure is always used for dust measurements.

For the measurement of gas concentrations the in-situ procedure has also been introduced in the meantime, even though the overwhelming majority of the installed measuring devices operate extractively. Measuring instruments, which measure across the channel cross-section, mostly deliver representative results. However there are also the types of in-situ measuring procedures which operate more or less at one point, such as oxygen measurement using the zirconium oxide process or dust/soot measurement using the scattered light principle.

In the case of extractive measuring technology the sample is taken from the most representative sampling point in the flue gas channel, the sample gas is then conveyed to the analysis system via a sample gas line and a sample gas conditioning system. According to the design of the system the measured values refer to dry or moist gas.

Whilst during the in-situ measurement of hazardous substances photometric processes are exclusively used, various different measuring principles are used with extractive sampling systems.

Tab. 2: Summary of measuring processes for waste incineration plants

Component	In-situ measurement	Extractive measurement
Dust	Extinction, scattered light measurement, tribo electricity	β absorption Scattered light measurement
SO ₂	NDIR NDUV	NDIR NDUV Conductivity
CO	NDIR	NDIR Electro-chemical cells
NO	NDIR NDUV	NDIR NDUV Chemiluminescence, electro-chemical cells
NO ₂	NDUV	NDUV Electro-chemical cells indirectly as NO after converter
HCl	NDIR	NDIR Conductivity, potentiometry
HF	-	Potentiometry
Hg	UV absorption (only metallic)	UV absorption (sum of metallic and ionic after reduction)
Total C	-	FID
O ₂	Electro-chemical cells (ZrO ₂)	Paramagnetism, electro-chemical cells - ZrO ₂

		-
Humidity	NDIR	NDIR FTIR Psychrometry O ₂ difference measurement (el. chem.)

The most significant measuring principles in Germany for qualified measuring devices are shown in the above table. As this summary shows photometric processes are used the most frequently.

In order to be able to monitor the limits shown in Tab. 1 measuring ranges of about 1.5 times the half-hour average value should be selected.

4. REQUIREMENTS FOR THE STABILITY OF ANALYSERS

Analysers are not absolute measuring instruments. They are set up before delivery by means of test gases or other standards. Through transportation, ageing and contamination, deviations and drift can occur both at the zero point as well as in their sensitivity which can lead to deviations in the readout. During continuous operation repeated resetting of the zero point and the sensitivity is therefore necessary at suitable intervals. For the operator this represents an additional cost factor which is put together from the investment for test gases and equipment as well as the handling and care of these gases.

Demands are regularly placed on the stability of analytical systems. In Germany for example the following maximum drifts should not be exceeded in the maintenance interval, whereby the maintenance interval should be a minimum of 8 days [7]

The zero drift shall not exceed
 $\pm 2\%$ (measuring range $\geq 20 \text{ mg/m}^3$) or
 $\pm 3\%$ (measuring range $\leq 20 \text{ mg/m}^3$)
of the readout range.

The time dependent drift of the reference point shall not exceed
 $\pm 2\%$ (measuring range $\geq 20 \text{ mg/m}^3$) or
 $\pm 3\%$ (measuring range $\leq 20 \text{ mg/m}^3$)
of the nominal value in the maintenance interval.

These requirements are valid for dust as well as for gas analysis instruments. Taking account of the low measuring ranges high demands are therefore placed on the stability of measuring instruments.

There is a fundamental difference between dust and all the gases. Dust is a component in which its specific character is influenced by a whole series of factors such as colour, density, grain size and reflective behaviour. Dust is not only different from plant to plant but it can also change within one plant because of different operating conditions. On the other hand gases represent well defined chemical measuring objects. NO_x can also be measured by conversion from NO₂ to NO. TOC is a special case, however by definition it is usually propane, which is selected as a reference component.

With reference to the setting of the measuring instruments this means that for gas analysers the components to be measured can fundamentally be provided in the form of a defined test gas.

For dust measuring instruments on the other hand there is no test dust which can mirror the properties of a plant-specific dust (to say nothing of the difficulty of manufacturing a "dust-containing test gas" and then conveying it to the analyser) which is only possible in special dust testing channels.

From this situation arose the need for introducing so-called adjustment aids for dust. For measuring instruments, which are used for gas components on the other hand both adjustment aids as well as test gas (reference material) can be used.

Adjustment aids and reference materials are defined in the VDI guideline 3950 [8].

Adjustment aids are substances, mixtures of substances or devices, whose interaction with the measuring method is known within certain limits and which have an effect either on the complete measuring procedure or on part of the measurement process in a different way as the measured object or act upon just a part of the measurement process in the same way as the measured object.

Amongst the different forms of adjustment aids are for example:

- Grid or glass filters for measuring devices, which are based on an optical measuring principle, or
- Standard solutions for measuring devices for the measurement of halogen compounds with the help of ion-sensitive electrodes.

Adjustment aids are used for the setting up or checking of the analyser's characteristics.

Reference materials are substances or mixtures of substances, for which the composition is known within given limits and for which one or more properties are so well established that they can be used for the calibration of a measuring instrument.

Amongst reference materials are for example the test gases which are used for setting up or checking the analyser's characteristics (see Section 2.9). For the complete measurement facility the test gases are only adjustment aids.

Test gases fundamentally form all the properties of the measured component in detail. Adjustment aids on the other hand only mirrors the properties of the measured component in a limited way.

4.1 Adjustment of the optical dust measurement systems

For the measurement of total dust there are optical, radio-metric and tribo-electrical processes available. For tribo-electrical measuring instruments there are no test standards, radiometric measuring systems, which are seldom used, can be manually set with test foils.

In general however optical dust measurement processes are used. All optical processes – even those for gas measuring instruments – operate according to the same fundamental principle: The beam from a light source is passed through the substance to be measured. Behind it is a light receiver which measures the intensity of the light. The absorption is a measure of the concentration of the substance to be measured. This principle is based on the Lambert-Beer Law. The overwhelming majority of optical dust measuring instruments operate in-situ and there is only a difference to be made between extinction measuring instruments and scattered light measuring instruments. In both cases the adjustment must be made by checking the zero point and then introducing an optical filter into the optical path. Triggering of

the control cycles and trimming takes place automatically, for example in 2 hour intervals. One significant cause of measuring instrument drift is contamination of the optical interfaces.

With this adjustment of the zero point and the reference point only the optical functionality of the system is guaranteed. There is thus still no correlation with the dust concentration which can only be achieved by comparative measurements with an independent dust measurement process.

4.2 Adjustment of gas measuring instruments

In continuous operation the adjustment of gas measuring instruments is carried out in general by means of the setting of the zero and reference points.

In the case of various other systems on the other hand once the initial setting of zero and reference points has been completed the regular follow-up adjustments are only made by resetting the zero point.

This adjustment of the zero point alone is only possible if the distance between the zero and reference point is stable and during subsequent adjustments of the zero point the reference point is also brought back to its setpoint. In principle an additional reference point check would be better. Zero point trimming alone is only possible then under the given preconditions if:

- No test gases are available for adjustment aids
- The test gases are unstable
- For cost reasons the intervals between the test gas injections should be as long as possible.

At defined intervals these systems must also be set up with test gas.

Adjustment of the devices can be manual or automatic. The increasing costs for the maintenance of measuring instruments has in the last decade further advanced the development of stable systems, which are automatically adjusted. In the following this development is described with various examples of extractive measuring technology.

4.2.1 Manual or automatic adjustment with flowing gases

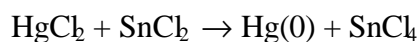
The simplest method of adjusting emission measuring devices is the manual injection of zero gas and test gas at regular intervals.

These gases are injected as closely as possible to the probe so as to ensure coverage of the complete measuring unit at the same time. Adjustment of the device then takes place directly on the analyser after a specific waiting time.

This manual injection of the test gas can also be automated. For this purpose the zero and test gases are connected to the sample gas pipe via solenoid valves. The injection then takes place successively in adjustable cycles. At the end of the zero and test gas injection the actual values are compared with the setpoints within the analyser. The essential requirement here is that the analysers must already be equipped with automatic adjusting units.

Normally test gases from pressure cylinders are used for this purpose, zero gas can also come from pressure cylinders, it is also however possible to use clean filtered ambient air which is drawn in by the pumps of the analysis system.

A special case is represented by the use of mercury test gases, which must be made on site. All mercury measuring instruments are equipped with a UV measuring cell and can only measure Hg (0). In practice however Hg (II) almost always occurs alongside Hg (0). In order to measure total mercury it is thus necessary to convert from Hg (II) to Hg (0) in front of the analyser. This can be done wet-chemically or by means of a thermocatalytic converter. To check the function of the analyser an Hg (0) test gas is therefore sufficient. This can be obtained in pressure cylinders, but for practical use there is too little experience with respect to the stability and accuracy of the certificates. Hg (0) test gases can be made by the steam pressure method or by the reduction of defined HgCl₂ solutions with stannic (II) chloride in an accurately defined carrier gas flow.



In order to test the reduction effect of the Hg (II) converter in front however a test gas is required, which contains Hg (II). This is best done by the evaporation of an aqueous HgCl₂ solution. Most suitable for this is the Hovacal test gas generator, which is discussed in another paper.

The stability of the Hg UV analyser in continuous operation is guaranteed by regular automatic zeroing, e.g. at hourly intervals.

4.2.2 Automatic adjustment with internal standards

15 years ago a similar development to the dust measuring devices had also begun in the case of gas analysis instrumentation, in that device adjustments were carried out by means of internal standards. These internal standards significantly reduce the need for flowing test gases.

Internal standards can be adjustment aids or internal reference materials, which only affect the analyser. In the case of gas analysers these internal reference materials have proved themselves well and have become generally accepted. They are used in photometers since the actual sensor does not come into direct interaction with the sample gas. Every medium, which causes a defined absorption of the light beam is in principle suitable for this. Whilst neither grids nor glass are selective, measuring cells filled with the sample gas are selective and are directly comparable with flowing test gases in their adjusting properties. A significant objection to the continuous use of cells was that only the analyser is adjusted.

The use of flowing test gases offers the advantage that the whole measuring system from the probe onwards can be included in the testing process.

Because however the tightness of the pipe system between probe and measuring instrument can be guaranteed today through the choice of up-to-date materials and connecting technologies, the adjustment of the analyser is normally suitable. The full drift behaviour therefore depends on the analyser.

For readjustment with internal standards it is always essential to set the zero point beforehand and to have a zero gas flow. If, such as in the case of SO₂, the cross-sensitivity to water vapour has to be considered then in the case of systems with coolers, the zero gas must be injected in front of the sample gas cooler. In this way it is ensured that the zero gas has the same water vapour pressure as the sample gas. More difficult than for photometric systems is the setting up of internal standards for systems, in which during measurement the sensor has to come into direct contact with the sample gas. Amongst such systems are for example measuring procedures which make use of thermal conductivity or electrochemical systems. It is only for oxygen measurement where the ambient air could be used as long as its O₂ concentration is sufficiently stable. In principle then the air must be treated as a flowing

test gas, but does not need to be stored beforehand. Therefore the use of internal standards is restricted to photometric processes [9].

Within the scope of emission measurements in the case of photometers it is only those with non-dispersive selection which can be used.

For NDUV and NDIR devices the use of gas-filled adjustment cells is described.

The adjustment cells are sealed silica glass cells, in which there is a given amount of the gas to be measured. The precondition for the long-term use of these glass cells is that the concentration of the measured component is absolutely constant in the cell. Since there are no specific requirements for the cells themselves it is necessary – as a minimum requirement – to make sure that they are at least as stable as test gas.

At the TÜV for South Germany, extensive tests were carried out on behalf of ABB Automation (previously Hartmann & Braun) on the long-term stability of these cells in connection with the measuring instruments: Radas and Uras 10. The tests were carried out for the components NO, CO, SO₂ and CO₂. The display readings on the cells were compared with flowing test gases. Initially during the tests, which were carried out at intervals of from 1 to 3 months, the zero point was set with flowing test gas as the reference point. Afterwards during renewed injection of the zero gas the readout values on the calibration cells were determined. At the same time the atmospheric air pressure was measured.

Since the analytical devices are open systems, the air pressure has an effect on the test gas reading. The closed cells are not influenced. In accurate comparisons it is therefore necessary to take the air pressure into account.

With the Radas measurements were carried out with cells filled with NO over about 4 years. In these measurements it was found that there was a long-term drift for the cells of 0.3 % of the nominal value in one year. The readout value was also not influenced by changing the lamp. Since the stability is only influenced by the cells they too can be used just as for the new Limas 11 (NO, SO₂, O₂) measuring instrument, which works according the same principle as Radas.

Measurements with the Uras 10 with cells for CO and CO₂ were carried out over 10 years for SO₂ and NO they extended over 7 years. In all cases the cell drift was also below 0.3% per annum.

With a system from the firm of Maihak similar results were obtained over a period of one year. Longer trials were presumably not carried out.

In the meantime these systems have proved themselves well in practice. The device adjustment takes place automatically at regular intervals. The personnel cost is reduced. Checking of the whole measurement facility with flowing gas is only necessary during the annual function test. During this the readout value of the cells is also checked and if necessary re-established. Particularly in the case of operators, who have no personnel who are trained in the handling of the analytical units, a better reliability can be achieved with the use of such systems.

Since the adjustment of O₂ measuring instruments also takes place automatically with the use of air oxygen as the reference gas, reliable and largely automated measuring systems are available for the measurement of CO, NO, SO₂ and O₂ in incineration plants. This development is all the more important for guaranteeing undisturbed emission control especially in the face of the ever more limited supplies of operating resources.

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